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Carbon−Sulfur Bond Cleavage and Hydrodesulfurization of Thiophenes by Tungsten

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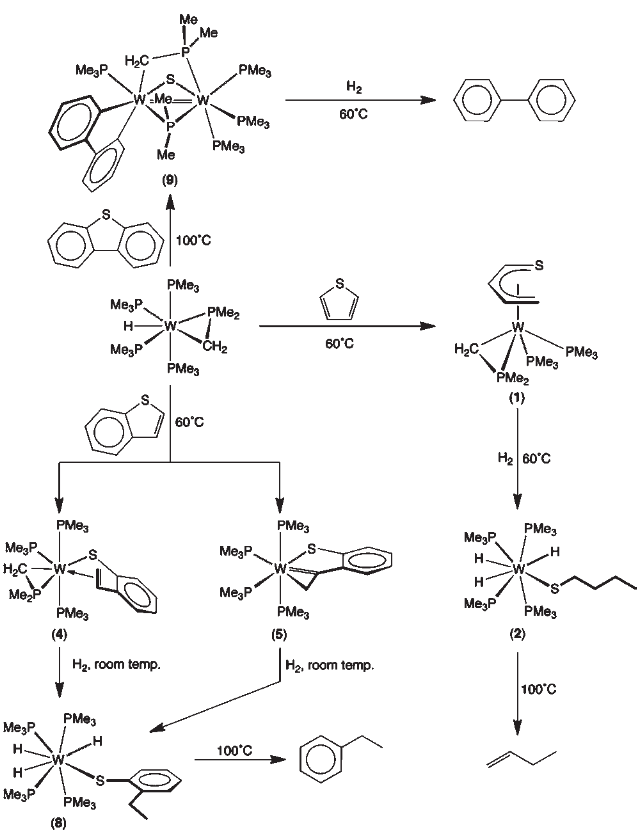
Supporting Information

ABSTRACT: The reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, $W(PMe_3)_5H_2$, $W(PMe_3)_4H_4$ and $W(PMe_3)_3H_6$ towards thiophenes reveal that molecular tungsten compounds are capable of achieving a variety of transformations that are relevant to hydrodesulfurization. For example, sequential treatment of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with thiophene and H_2 yields the butanethiolate complex, $W(PMe_3)_4(SBu^n)H_3$, which eliminates but-1-ene at 100 °C. Likewise, sequential treatment of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with benzothiophene and H_2 yields $W(PMe_3)_4(SC_6H_4Et)H_3$, which releases ethylbenzene at 100 °C. Moreover, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ desulfurizes dibenzothiophene to form a dibenzometallacyclopentadiene complex, $[(\kappa^2\text{-}C_{12}H_8)W(PMe_3)](\mu\text{-}S)(\mu\text{-}CH_2PMe_2)(\mu\text{-}PMe_2)[W(PMe_3)_3]$.

Hydrodesulfurization (HDS) is the essential process for removing sulfur-containing impurities from crude petroleum in order to obtain (i) cleaner fuels that minimize environmental pollution and (ii) cleaner chemical feedstocks that are less likely to poison the catalysts that are used for subsequent transformations.[1−3] The catalysts employed for hydrodesulfurization are largely composed of molybdenum and tungsten sulfides supported on alumina, and much effort has been directed towards enhancing the efficiency of this process. It is difficult, however, to achieve a molecular level understanding of the catalytic cycle in view of the fact that the catalysts are heterogeneous.[4] For this reason, the reactivity of sulfur-containing compounds towards the metal centers of various molecular systems has been the focus of much attention.[5,6] However, despite the fact that molybdenum and tungsten are the most important components of HDS catalysts,[1,2,3] the majority of these studies has focused on precious metals such as rhodium, iridium, palladium and platinum.[5,6] Therefore, we describe here the first report of desulfurization of thiophenes by molecular tungsten compounds.

We have previously demonstrated that $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is a highly reactive molecule that is capable of achieving a variety of bond activation reactions, as exemplified by the cleavage of an aromatic C−C bond in quinoxaline.[7] On this basis, we have investigated the reactivity of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ towards thiophenes and have thereby discovered that it is capable of cleaving the C−S bonds of thiophene, benzothiophene and dibenzothiophene, as illustrated in Scheme 1.[8] For example, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with thiophene at 60 °C to give the butadiene−thiolate complex $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (**1**), as illustrated in Scheme 1.[9] The formation of $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (**1**) represents the first example of thiophene C−S bond cleavage and hydrogen transfer by a molecular tungsten compound.[10] Furthermore, the butadiene−thiolate ligand of $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (**1**) may be hydrogenated at 60 °C to give the butanethiolate complex, $W(PMe_3)_4(SBu^n)H_3$ (**2**),[11−13] which liberates but-1-ene upon thermolysis at 100 °C (Scheme 1). As such, these observations demonstrate that a molecular tungsten compound is capable of achieving key steps in the hydrodesulfurization of thiophene.

Scheme 1



It is pertinent to compare the above reactivity with that of the corresponding molybdenum system[14,15] because there are some distinct differences. In particular, whereas only the butadiene−thiolate complex $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (**1**) has

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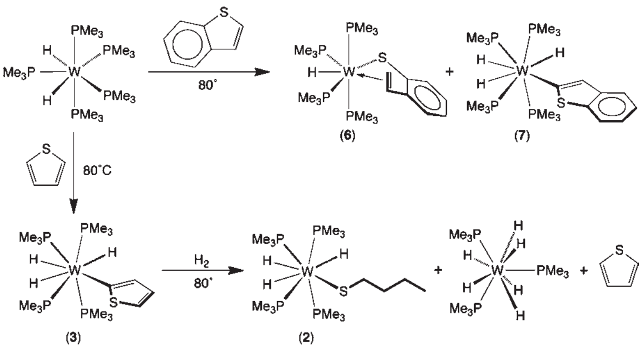
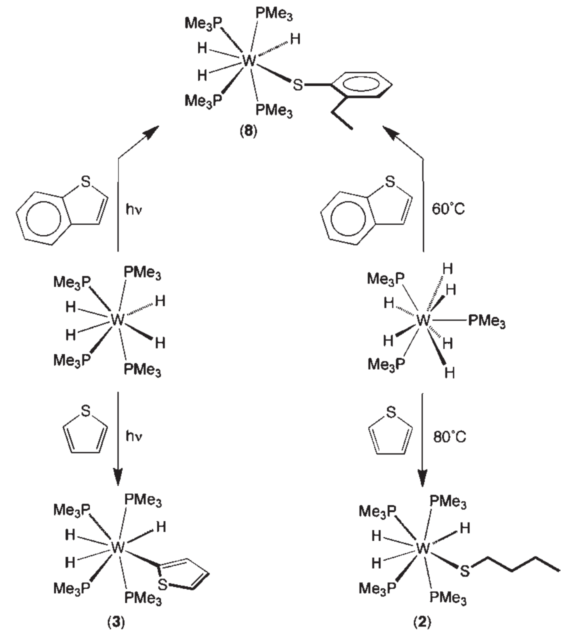
Scheme 2



Scheme 3



been isolated for the tungsten system, the reaction of Mo(PMe$_3$)$_6$ proceeds readily at room temperature to give the metallathiacycle, (κ^2-C,S-C$_4$H$_4$S)Mo(PMe$_3$)$_4$, which rapidly converts to the butadiene−thiolate complex (η^5-C$_4$H$_5$S)Mo(PMe$_3$)$_2$(η^2-CH$_2$PMe$_2$) *and* the η^5-thiophene derivative (η^5-C$_4$H$_4$S)Mo(PMe$_3$)$_3$.[14a,b] Another interesting difference is that, whereas the tungsten butadiene−thiolate complex (η^5-C$_4$H$_5$S)W(PMe$_3$)$_2$(η^2-CH$_2$PMe$_2$) (**1**) is readily hydrogenated to the butanethiolate complex W(PMe$_3$)$_4$(SBu^n)H$_3$ (**2**) at 60 °C, the molybdenum counterpart (η^5-C$_4$H$_5$S)Mo(PMe$_3$)$_2$(η^2-CH$_2$PMe$_2$) does not react with H$_2$ under the same conditions. Thus, although the formation of the butadiene−thiolate complex from the reaction of thiophene with the molybdenum complex Mo(PMe$_3$)$_6$ is more facile than that for the reaction of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H, hydrogenation of the butadiene−thiolate ligand occurs more readily for the tungsten system.

In view of the fact that hydrogenation is an important component of hydrodesulfurization, we have also investigated the reactivity of the series of hydride complexes, W(PMe$_3$)$_5$H$_2$, W(PMe$_3$)$_4$H$_4$ and W(PMe$_3$)$_3$H$_6$, towards thiophene (Schemes 2 and 3). Significantly, these hydride complexes exhibit different reactivity from that of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H. For example, W(PMe$_3$)$_5$H$_2$ reacts with thiophene to give the κ^1-thienyl complex, W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) (Scheme 2),[16] a complex that is also generated by the photochemical reaction of thiophene with W(PMe$_3$)$_4$H$_4$ (Scheme 3).[17,18] In contrast, thiophene reacts with W(PMe$_3$)$_3$H$_6$ to give the butanethiolate complex W(PMe$_3$)$_4$(SBu^n)H$_3$ (**2**), as illustrated in Scheme 3.[19]

The fact that W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H and W(PMe$_3$)$_5$H$_2$ behave differently towards thiophene suggests that the reactions do not occur *via* a common [W(PMe$_3$)$_5$] intermediate. It is, therefore, postulated that, whereas the reaction of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H proceeds *via* [W(PMe$_3$)$_5$], the reaction of W(PMe$_3$)$_5$H$_2$ involves initial dissociation of PMe$_3$ to give 16-electron [W(PMe$_3$)$_4$H$_2$] followed by oxidative addition of a thiophene C−H bond. As such, it is suggested that cleavage of the C−S bond, relative to a C−H bond, is more favored for [W(PMe$_3$)$_5$] than [W(PMe$_3$)$_4$H$_2$].

The formation of the κ^1-thienyl complex W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) is also noteworthy because the corresponding reaction of the molybdenum counterpart Mo(PMe$_3$)$_5$H$_2$ with thiophene does not yield Mo(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$, but rather gives a mixture of the η^5-thiophene and butadiene−thiolate complexes, (η^5-C$_4$H$_4$S)Mo(PMe$_3$)$_3$ and (η^5-C$_4$H$_5$S)Mo(PMe$_3$)$_2$(η^2-CH$_2$PMe$_2$).[14b] Thus, the molybdenum system exhibits a greater propensity to cleave the C−S bond of thiophene than does the tungsten system. We postulate that the origin of this difference is that the tungsten κ^1-thienyl complex W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) represents a kinetic product that is also of sufficient thermodynamic stability to inhibit access to an intermediate that is capable of achieving C−S bond cleavage.

In support of this suggestion, treatment of Mo(PMe$_3$)$_5$H$_2$ with d_4-thiophene is accompanied by incorporation of hydrogen into the α-position of free thiophene prior to formation of the η^5-thiophene and butadiene−thiolate complexes,[14b] whereas no such exchange is observed for W(PMe$_3$)$_5$H$_2$. Furthermore, W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) does not react with PMe$_3$ to regenerate W(PMe$_3$)$_5$H$_2$. These observations, therefore, are consistent with facile reversible oxidative addition of the C−H bond of thiophene to molybdenum, but irreversible (on the timescale of the experiment) oxidative addition to tungsten.

Although the evidence presented above indicates that W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) does not undergo facile reductive elimination of thiophene, elimination of thiophene may be induced by treatment of W(PMe$_3$)$_4$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_3$ (**3**) with H$_2$, a reaction that is also accompanied by the formation of W(PMe$_3$)$_3$H$_6$ and the butanethiolate complex, W(PMe$_3$)$_4$(SBu^n)H$_3$ (**2**), as illustrated in Scheme 2. Relative to W(PMe$_3$)$_4$(SBu^n)H$_3$, the formation of W(PMe$_3$)$_3$H$_6$ and thiophene is inhibited by PMe$_3$, thereby suggesting that the reductive elimination of thiophene presumably occurs *via* a higher-valent species such as W(PMe$_3$)$_3$(κ^1-C$_\alpha$-C$_4$H$_3$S)H$_5$, obtained by dissociation of PMe$_3$ and oxidative addition of H$_2$. The formation of the butanethiolate complex W(PMe$_3$)$_4$(SBu^n)H$_3$ (**2**) in this reaction is interesting because it demonstrates that although W(PMe$_3$)$_5$H$_2$ itself does not allow isolation of a product derived from C−S bond cleavage, such a species may be obtained upon subsequent treatment with H$_2$ (Scheme 2).[20]

The reactivity of W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H, W(PMe$_3$)$_5$H$_2$, W(PMe$_3$)$_4$H$_4$ and W(PMe$_3$)$_3$H$_6$ towards other thiophenes has also been investigated. For example, W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H reacts with benzothiophene to give a mixture of products that includes isomeric (κ^1,η^2-CH$_2$CHC$_6$H$_4$S)W(PMe$_3$)$_3$(η^2-CH$_2$PMe$_2$) (**4**) and (κ^1,η^2-CH$_2$CC$_6$H$_4$S)W(PMe$_3$)$_4$ (**5**) (Scheme 1).

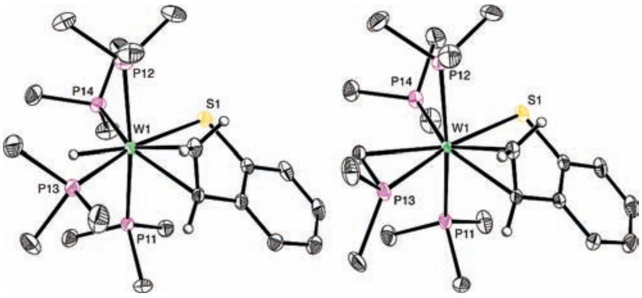


Figure 1. Molecular structures of $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_4H$ (**6**) (left) and $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**4**) (right).

Interestingly, the corresponding reaction of $W(PMe_3)_5H_2$ with benzothiophene gives a different pair of isomers, namely $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_4H$ (**6**) and $W(PMe_3)_4(\kappa^1\text{-}C_\alpha\text{-}CCHSC_6H_4)H_3$ (**7**) (Scheme 2), that feature two more hydrogen atoms than the products obtained from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$.[21] Thus, $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_4H$ (**6**) is formally related to $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**4**) by addition of H_2 across the W—C bond, and is otherwise structurally very similar (Figure 1).

$(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**4**), $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)W(PMe_3)_4$ (**5**) and $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_4H$ (**6**) react with H_2 at room temperature to give the arylthiolate $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**) (Scheme 1), which has been structurally characterized by X-ray diffraction (Figure 2). Furthermore, $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**) is also obtained upon treatment of benzothiophene with $W(PMe_3)_4H_4$ and $W(PMe_3)_3H_6$, although the former requires photochemical activation (Scheme 3).[22] Of most interest, however, upon heating, $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**) eliminates ethylbenzene (Scheme 1), the principal product of hydrodesulfurization.[23,24] As such, the reactivity exhibited by this tungsten system provides a series of steps by which benzothiophene may be hydrodesulfurized.[13]

Significantly, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is also capable of desulfurizing dibenzothiophene, a compound that is most resistant to hydrodesulfurization.[5] Specifically, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with dibenzothiophene to give the dinuclear dibenzometallacyclopentadiene complex, $[(\kappa^2\text{-}C_{12}H_8)W(PMe_3)](\mu\text{-}S)(\mu\text{-}CH_2PMe_2)(\mu\text{-}PMe_2)[W(PMe_3)_3]$ (**9**) (Scheme 1),[25] which has been structurally characterized by X-ray diffraction (Figure 3). While C—S bond cleavage of dibenzothiophene is precedented, reactions that involve desulfurization are rare.[5,26,27] Indeed, there is only one other structurally characterized complex listed in the Cambridge Structural Database that features a κ^2-biphenyldiyl ligand derived from dibenzothiophene, namely a nickel compound synthesized by Jones.[26,28] In addition, treatment of the dibenzometallacyclopentadiene complex, $[(\kappa^2\text{-}C_{12}H_8)W(PMe_3)](\mu\text{-}S)(\mu\text{-}CH_2PMe_2)(\mu\text{-}PMe_2)[W(PMe_3)_3]$ (**9**) with H_2 at 60 °C liberates biphenyl (Scheme 1).

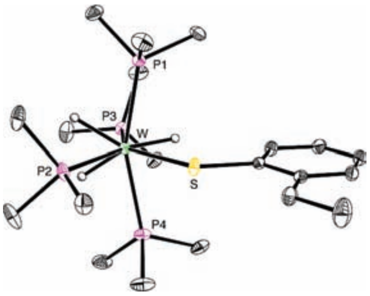


Figure 2. Molecular structure of $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**).

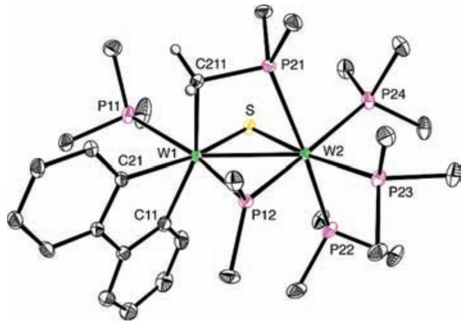


Figure 3. Molecular structure of $[(\kappa^2\text{-}C_{12}H_8)W(PMe_3)](\mu\text{-}S)(\mu\text{-}CH_2PMe_2)(\mu\text{-}PMe_2)[W(PMe_3)_3]$ (**9**).

Although we have not isolated any products from the reactions of either $W(PMe_3)_5H_2$, $W(PMe_3)_4H_4$ or $W(PMe_3)_3H_6$ with dibenzothiophene, the latter two do, nevertheless, serve as effective catalysts for the exchange of deuterium and hydrogen between dibenzothiophene and C_6D_6.[29] For example, $W(PMe_3)_3H_6$ catalyzes exchange into the α positions at 60 °C, the β and γ positions at 80 °C, while the δ site remains undeuterated.[30,31]

In conclusion, the reactivity of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, $W(PMe_3)_5H_2$, $W(PMe_3)_4H_4$ and $W(PMe_3)_3H_6$, towards thiophenes has demonstrated that tungsten centers are capable of achieving a variety of transformations relevant to hydrodesulfurization. For example, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ cleaves the C—S bond of thiophene to give the butadiene—thiolate complex, $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (**1**), that may be subsequently hydrogenated to the butanethiolate complex, $W(PMe_3)_4(SBu^n)H_3$ (**2**), which, upon heating, liberates but-1-ene. $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ also cleaves the C—S bond of benzothiophene to give isomeric $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (**4**) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)W(PMe_3)_4$ (**5**). Both of these complexes may be hydrogenated at room temperature to give the arylthiolate $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**) which, upon heating, liberates the hydrodesulfurization product, ethylbenzene. Finally, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is also capable of desulfurizing dibenzothiophene to form a dibenzometallacyclopentadiene complex, $[(\kappa^2\text{-}C_{12}H_8)W(PMe_3)](\mu\text{-}S)(\mu\text{-}CH_2PMe_2)[W(PMe_3)_3]$ (**9**), which liberates biphenyl upon heating in the presence of H_2. The structural characterization of these compounds, together with their interconversions, provides a foundation for analyzing the reactions that occur on tungsten-based HDS catalysts.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, computational data and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) All new compounds, with the exception of $W(PMe_3)_4(SBu^n)H_3$ and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)W(PMe_3)_4$, have been structurally characterized by X-ray diffraction.

(9) Isotope-labeling studies employing d_4-thiophene indicate that formation of molybdenum and tungsten butadiene-thiolate compounds $(\eta^5\text{-}C_4H_5S)M(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ from $Mo(PMe_3)_6$ (ref 14a) and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ occurs *via* a similar mechanism, with the hydrogen from the PMe_3 ligand terminating in the site adjacent to sulfur.

(10) Moreover, even examples of simple coordination[10a−10e] and C−S bond cleavage[11f,g] of thiophenes are rare for tungsten. See: (a) Reynolds, M. A.; Guzei, I. A.; Logsdon, B. C.; Thomas, L. M.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1999**, *18*, 4075–4081. (b) Delafuente, D. A.; Myers, W. H.; Sabat, M.; Harman, W. D. *Organometallics* **2005**, *24*, 1876–1885. (c) Schultz, R. H. *Organometallics* **2004**, *23*, 4349–4356. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294–2301. (e) Stolz, I. W.; Haas, H.; Sheline, R. K. *J. Am. Chem. Soc.* **1965**, *87*, 716–718. (f) Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448–4452. (g) Mills, R. C.; Abboud, K. A.; Boncella, J. M. *Chem. Commun.* **2001**, 1506–1507.

(11) Evidence for the presence of the butanethiolate ligand is provided by the fact that treatment of $W(PMe_3)_4(SBu^n)H_3$ with $PhCO_2H$ immediately liberates Bu^nSH.

(12) For other examples of hydrogenation of thiophene and benzothiophene to butanethiolate and ethylphenylthiolate ligands, respectively, see: (a) Vicic, D. A.; Jones, W. D. *Organometallics* **1997**, *16*, 1912–1919. (b) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767–10775.

(13) For examples of desulfurization of thiophene and benzothiophene by other metals, see ref 14b and references therein.

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(17) The reaction is also accompanied by the formation of $W(PMe_3)_3H_6$ due to reaction of $W(PMe_3)_4H_4$ with the H_2 that is liberated.

(18) $W(PMe_3)_4H_4$ also serves as a catalyst for the photochemical exchange of hydrogen and deuterium between both the α- and β-positions of thiophene and C_6D_6. The isotopic exchange, however, is inhibited by PMe_3, which suggests that the reaction may occur *via* reversible oxidative addition of benzene and thiophene C−H(D) bonds to 16-electron $[W(PMe_3)_3H_4]$, rather than to $[W(PMe_3)_4H_2]$.

(19) This transformation is necessarily accompanied by ligand redistribution. In an attempt to increase the yield of $W(PMe_3)_4(SBu^n)H_3$, the reaction between $W(PMe_3)_3H_6$ and thiophene was performed in the presence of PMe_3. However, under these conditions, only $W(PMe_3)_4H_4$ (which is thermally unreactive towards thiophene) was obtained.

(20) Among other mechanisms, the formation of $W(PMe_3)_4(SBu^n)H_3$ could possibly take place *via* C−S bond cleavage of the κ^1-thienyl ligand. For an example of such cleavage of a κ^1-thienyl ligand at a ditungsten center, see: Chisholm, M. H.; Haubrich, S. T.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 1634–1647.

(21) The formation of $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_4H$ and $W(PMe_3)_4(\kappa^1\text{-}C_\alpha{-}CCHSC_6H_4)H_3$ also provides another interesting contrast with the molybdenum system, for which $Mo(PMe_3)_5H_2$ reacts with benzothiophene to give $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)Mo(PMe_3)_4$. See ref 14b.

(22) $W(PMe_3)_4(SC_6H_4Et)H_3$ (**8**) can also be formed directly by reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with benzothiophene in the presence of H_2.

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(24) The tungsten- and sulfur-containing products are presently unknown.

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(29) $W(PMe_3)_4H_4$ requires photochemical activation to catalyze the exchange.

(30) The α site is closest to the sulfur atom.

(31) In support of these observations, DFT calculations on the computationally simpler system in which the methyl groups of the PMe_3 ligands are replaced by hydrogen atoms indicate that the δ isomer of $W(PH_3)_4(\kappa^1\text{-}C{-}C_6H_3SC_6H_4)H_3$ is more than 10 kcal mol^{-1} less stable than the α, β and γ isomers.